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THE PURIFICATION AND PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS I. THE INTERPRETATION OF TIME-TEMPERATURE CURVES IN FREEZING POINT DETERMINATIONS AND AS A CRITERION OF PURITY.

BY EVALD L. SKAU.

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(Continued from page 3 of cover.)

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By Evald L. Skau.

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THE PURIFICATION AND PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS I. THE INTERPRETATION OF TIME-TEMPERATURE CURVES IN FREEZING POINT DETERMINATIONS AND AS A CRITERION OF PURITY.[1]

By Evald L. Skau.[2]

The need for a sound and practical criterion of purity for organic *liquid* compounds has long been very evident. Such a criterion is of fundamental importance in any investigation which requires the use of highly pure materials; for example, in the exact determination of physical constants. The method here described and which we shall classify with what we shall call "*non-comparative criteria* of purity" is applicable to all organic compounds which can be made to crystallize and whose melting points lie between liquid air temperature and about 250° C.

The methods now most generally in use for the estimation of the purity of *liquids* are unsatisfactory and indefinite. A comparison of some physical constant or constants, such as density, boiling point, viscosity, refractive index, or freezing point, with the accepted values in the literature presupposes that the latter values were accurately determined on pure materials, a supposition which is seldom warranted but often made. Another test of purity applied to liquids is the constancy of the values for these physical constants during a fractional distillation. The frequent occurrence of azeotropic mixtures,[3] however, renders this method very untrustworthy. Probably the most satisfactory test now in use is the constancy of the temperature during freezing but this as ordinarily carried out can not be considered a good criterion of purity since the size of the sample used, the relative temperature of the surroundings, and other factors

[1] Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 252.

[2] National Research Fellow (1926–28).

This paper was written during the tenure of a Guggenheim Fellowship at the Universities of Munich and Frankfort a. Main and the Bureau International des Étalons Physico-Chimiques, Brussels.

[3] See the long series of papers by Lecat, Ann. Soc. Scient. Bruxelles (1926–1930), and also his book, "L'Azeotropisme," Brussels (1918).

have not been properly standardized.[4] Furthermore, great experimental difficulties are usually encountered in applying this method when the liquid in question is hygroscopic or absorbs carbon dioxide from the atmosphere.

[4] The length of the flat, $(t_2 - t_1)$, on a cooling curve, that is, the length of time taken for the sample to drop through the smallest temperature range detectable with the thermometer used, $(\theta_2 - \theta_1)^\circ$, is a function of many variables. This follows from a consideration of Newton's Law of Cooling assuming ideal radiation and true equilibrium throughout.

Newton's Law states that

$$\frac{dH}{dt} = aK\,(\theta - \theta_s) \tag{1}$$

where H is the heat content of the sample, a is the area of its radiating surface, K is a constant depending on the particular set-up, and θ and θ_s are the temperatures of the sample and of the surroundings respectively. But

$$dH = mCd\theta \tag{2}$$

where m is the weight of the sample and C is its specific heat over the small temperature range in question (involving the heat of fusion per gram of the substance). Therefore

$$\frac{d\theta}{dt} = \frac{aK}{mC}\,(\theta - \theta_s). \tag{3}$$

As a first approximation we can consider a, K, m, and C as constants for a given set-up over the small temperature range θ_2 to θ_1. Under these conditions equation (3) can be integrated and rearranged to give

$$t_2 - t_1 = \frac{mC\,(\theta_2 - \theta_1)}{aK\,(\theta - \theta_s)} \tag{4}$$

That is, the length of the flat varies proportionally as m, C, and $(\theta_2 - \theta_1)$, and inversely as a, K and $(\theta - \theta_s)$.

The following facts also should be noted: a is a function not only of m but also of the shape and dimensions of the sample tube; and the amount of impurity causing the drop in the temperature of the sample from θ_2 to θ_1 is also a function of the heat of fusion of the sample (from the van't Hoff Equation,

$$\frac{dln\,x}{d\theta} = \frac{\Delta H}{R\theta^2},$$

where x is the mole fraction of the form crystallizing out, ΔH is its heat of fusion, and $R = 1.99$ cals.).

From these considerations it is evident that *the length of the flat can be varied almost at will* by choosing the proper conditions.

In the case of *solids*, on the other hand, considerable progress has been made toward estimating purity but, unfortunately, it is not always given due consideration. The comparison of the freezing point, alone or along with other physical properties, with the values recorded in the literature is many times considered sufficient. The failure to change the freezing point by successive recrystallization of the compound from a variety of solvents is probably the most common and satisfactory general criterion used. It must be borne in mind, however, that its sensitivity depends on the efficiency of the recrystallization, and especially, on the accuracy of the freezing point determination, and the completeness of the removal of the solvent.

In the case of solids as in the case of liquids, a "long flat" on the cooling curve is no proof of high purity unless it is referred to the time required for *complete* freezing under standardized conditions.[5]

Non-Comparative Criteria of Purity. The various criteria of purity can be divided into two classes: *comparative criteria* and *non-comparative criteria.* By a *comparative criterion* we mean one which depends on the comparison of one or more properties of the sample (a) with those obtained by other authors or (b) with those obtained for other samples which have been gotten by some fractionating process. By a *non-comparative criterion of purity,* on the other hand, we mean one by which the estimation of purity involves the measurements made on the original sample only; in this case the only comparison is with a standard or an ideal which is supposedly the same for all pure substances.

All the methods mentioned above are of the comparative type, with the exception of the length of the flat on a cooling curve, this being a rather inefficient form of a non-comparative method. Let us now consider these non-comparative methods since the method here described falls in that class.

Perhaps the most positive single evidence of purity can be obtained from the shape (1) of the volume-temperature curve at constant pressure, (2) of the volume-pressure curve at constant temperature, or (3) of the heat content-temperature curve, when they are determined by a static or integral method in the region where solid changes to liquid. In fact these curves may be used to estimate the amount

[5] See Hüttner and Tammann, Z. anorg. Chem., *43*, 218 (1905); White, Amer. Jour. Sci., [4], *28*, 453 (1909), Z. anorg. Chem., *69*, 305 (1911); and Andrews, Kohman and Johnston, J. Phys. Chem., *29*, 914 (1925).

of impurities present.[6] Serious experimental difficulties are involved in getting the data for the isotherm or the isobar, however, so that the specific heat method, (3), is probably the best of the three. Unfortunately this method is likewise unsuitable for a general laboratory method for estimating purity, due to the excessive time required to get the necessary data.

Johnston and coworkers,[7] however, studied the cooling curves obtained in a special apparatus in the case of solid compounds which had been proved to be sufficiently pure for their specific heat determinations, and found that the flat (constancy of temperature within 0.10°) lasted until the sample was three-quarters solidified.

In the basis of this work and that of White,[8] we have constructed a time-temperature-curve apparatus which is applicable to solids and liquids whose freezing points lie above liquid air temperature and we have made a study of the effects of small amounts of impurity not only on cooling curves but also on heating curves. A comparison of the curves so obtained brings out the fact that the nature of the flat obtained is only one of the characteristics which can be used to detect the impurity, and that it is, in fact, probably neither as reliable nor as sensitive as the nature of the end of the completed cooling curve and especially the nature of the approach to the flat in the heating curve when the conditions are properly standardized. We are also able to point out many advantages of the use of heating curves over the use of cooling curves as a criterion.

The distinct advantage of this time-temperature-curve method for the detection of impurities is that it is a non-comparative method so that, within certain limits to be mentioned, the results obtained for a single sample are conclusive in themselves even though the history of the sample be unknown.

The apparatus here described can be used over a wide range of temperatures and the sample may be handled entirely in vacuo, so that absorption of moisture, carbon dioxide or oxygen from the atmosphere may be eliminated. The apparatus may also be used for the determination of freezing points and transition points at atmospheric pressure or in vacuo.

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[6] Tammann, "Aggregatzustände," Verlag von Leopold Voss, Leipzig (1922) pages 83–90; Block, Z. phys. Chem., *78*, 385 (1912); Bogojawlenski, Schr. d. Dorpeten Naturf. Ges., *13*, 1 (1904); Andrews, Lynn and Johnston, Jour. Amer. Chem. Soc., *48*, 1274 (1926).

[7] Andrews, Kohman and Johnston, *loc. cit.*; Andrews, Lynn and Johnston, *loc. cit.*

[8] White, Z. anorg. Chem., *69*, 305 (1911); J. Phys. Chem., *24*, 393 (1920).

Apparatus.

The apparatus (see Figure 1) consists essentially of a cooling curve apparatus similar to that previously described,[9] set in an air cryostat which is similar in principle to that used by Keyes and his co-workers.[10]

The sample, 0.5 to 0.7 grams, is hermetically sealed in a specially constructed tube, A, (about 3 cm. long) made of very light 5.5 to 6.5 mm. glass tubing (about 0.07 mm. wall thickness),[11] in order that its heat capacity may be negligibly small with respect to that of the sample, and so constructed that the temperature of the sample may be read by means of a single-junction thermocouple, one element of which, G, fits snugly into a thin-walled capillary tube, N, containing some fluid (ether, CCl_4 or vaseline, as the case may be), and extending down through the center of the sample to within about 4 mm. of the bottom. The sample tube is fastened by means of a wire (not shown in the diagram) to two little knobs protruding from the sides of the thin-walled glass tube K through which the thermoelement enters. This tube extends up through the loosely fitting fibroid stopper L, which is connected in turn with the long fibroid handle M, by means of which the whole may be removed from the apparatus. A wad of cotton, P, is pressed into the mouth of the flask to keep out moisture.

The sample tube is suspended in the shield B, which is a hollow copper cylinder closed at the bottom and wound with a 30-ohm Nichrome resistance H. The latter is insulated from the copper by a thin layer of mica and connected to a variable source of current. The thermoelement, F, runs down through the 1.5 mm. hole, drilled longitudinally, and the junction is silver-soldered into a transverse hole opposite the sample as shown in the diagram.

The shield is set on a mat of shredded asbestos in C, an unsilvered double-walled vessel (length, 45 cm.; inside diameter, 4.5 cm.), so connected through tube E with a mercury diffusion pump and a gas reservoir that the pressure between its walls may be varied at will. D is a silvered Dewar tube with a transparent longitudinal slit so set that the sample is visible through a corresponding slit (6 by 25 mm.) through the shield, a suitable light being placed behind the apparatus. C is held in place partly by the cork O at the bottom and partly by a

[9] Skau and Saxton, Jour. Amer. Chem. Soc., *50*, 2693 (1928).

[10] Taylor and Smith, Jour. Amer. Chem. Soc., *44*, 2450 (1922); Keyes, Taylor and Smith, Jour. Math. Phys. Mass. Inst. Tech., *1*, 211 (1922). See also Cardoso, Jour. chim. phys., *15*, 317, (1915).

[11] "Wafer weight" or "Friable" Tubing, No. 50105, obtainable from Kimble Glass Co., Vineland, New Jersey, U. S. A.

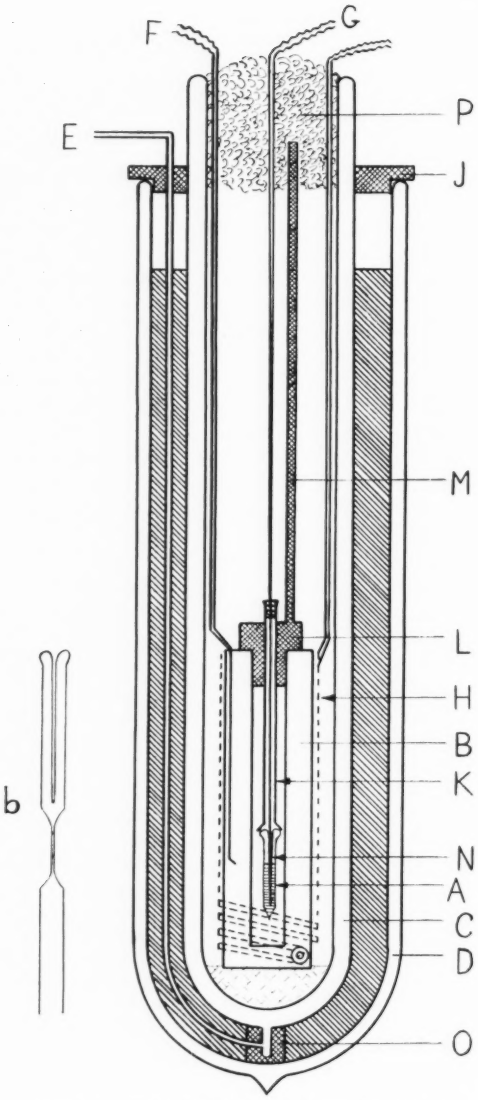

FIGURE 1. Time-Temperature Curve Apparatus.

ring of transite board, J, stuck fast to the glass with Khotinski cement and fitting loosely in the mouth of D.

The temperature of the shield and of the melt were read by means of the thermoelements F and G respectively (cold junctions at 0°) the measurements being made to the nearest microvolt, about 0.03°, with a Leeds and Northrup Type K potentiometer. Both thermocouples were constructed of No. 36 copper and No. 30 constantan, B & S gauge. Thermocouple G was calibrated at the freezing point of water, the freezing point of mercury (− 38.87°), the sublimation point of carbon dioxide (− 78.51°), and at the boiling point of liquid oxygen (− 183.00°).[12] The last two points were established by measuring the vapor pressure of the carefully purified substances in a constant temperature cryostat in which the thermoelement was immersed.[13] In each case the purity of the sample was tested by evaporating to one-half volume and then redetermining the vapor pressure. The calibration at the mercury point was carried out in the same apparatus and under the same conditions as the chlorobenzene samples.

Procedure.

Filling the Sample Tube. The sample tube is thoroughly cleaned with boiling concentrated nitric acid, well rinsed, and dried by heating in vacuo, before the constriction is made as shown in Figure 1, b. The procedure for filling depends somewhat on the purpose of the experiment. If it is desired to test a certain substance without further purification and it has already been exposed to the atmosphere, or if, as in the case of the samples used for this investigation, exposure to the atmosphere for a short time has no appreciable effect, the substance may simply be poured into the tube. Otherwise the sample is introduced into an all-glass apparatus with or without some purifying or drying agent, and, after evacuation, condensed into the sample tube which is meanwhile dipped in liquid air. In any case, in sealing off the sample tube all precautions should be taken to avoid overheating the sample even in the vapor state; it is thus advisable to cool the sample in liquid air while gently heating the constriction before sealing, the upper part of the tube being meanwhile stoppered or connected with a vacuum as the case may be.

[12] "International Critical Tables," New York, Volume I, page 53.

[13] The details of this method have been fully described by Keyes, Townshend and Young, J. Math. Phys. Mass. Inst. Tech., *1*, 302, (1922); see also Loomis and Walters, Jour. Amer. Chem. Soc. *48*, 3101 (1926), and Henning, Ann. Physik, *43*, 282 (1914).

Adjustment of the Apparatus. To obtain a heating or a cooling curve for a substance whose freezing point is below room temperature, flask D is filled with liquid air, and dry CO_2-free air is admitted through E. The temperature of the shield falls rapidly until at the proper time the space between the walls of the vessel C is evacuated.[14] By adjustment and occasional readjustment of the voltage applied across the terminals of the heater, H, the temperature of the shield is now caused to rise or fall at the desired constant rate, which is maintained throughout the curve (from 0.3 to 0.5° per minute for cooling curves and from 0.25 to 0.35° for heating curves). Readings of the melt temperature are recorded for every minute and, during the more important parts of the curve, for every half-minute; readings of the shield temperature are made for every minute at first but later only occasional readings are necessary.

Cooling Curves. The shield temperature should be started from two to three degrees above the temperature at which the crystallization is to be started, so that the rate of fall of the shield and the melt is then roughly the same. Crystallization is then initiated by twirling the sample tube in the apparatus for a few seconds. This can be done by rapidly rolling the upper end of the fibroid handle, M, between the thumb and the index finger after first lifting it about one centimeter. If there is a sudden rise in temperature, this twirling is repeated occasionally during the next minute to ensure dissemination of the crystals which have formed throughout the melt. If there is no break, however, the sample is allowed to cool through another 0.5° before repeating the procedure. After crystallization has thus been started, readings are continued, *without stirring the sample*, until the temperature of the melt has again come to within two or three degrees of the shield temperature, which, in the meanwhile, has been kept falling at the initial rate. Due to the absence of stirring after the first minute, it is desirable to supercool the sample to a temperature from three to five degrees below the freezing point before starting the crystallization as will be explained later.

The above method of starting the crystallization sometimes fails. A more generally applicable method is to remove the sample tube from the apparatus, by means of the fibroid handle, M, dip the very tip of

[14] This evacuation of flask C is not absolutely necessary. If it were not evacuated, the radiation from the shield would be more rapid; therefore, more heat would have to be supplied by the heater to establish the desired rate of fall or rise, and a corresponding amount of liquid air would be wasted.

the tube in liquid air for a fraction of a second, and reinsert it in the apparatus, the whole process being completed in two or three seconds.[15] The sample tube is then twirled during the first minute to mix the crystals with the supercooled liquid as above. This was the method used for obtaining the curves reported here.

Heating Curves. The shield is first cooled to 3° or 4° below the freezing point, as determined by a rough preliminary cooling curve, and kept constant at this temperature. The sample is then completely frozen and inserted in the apparatus at a considerably lower temperature. When the sample has come to within 0.1°–0.2° of the temperature of the shield the latter is caused to rise at the desired rate, which is maintained throughout the curve.[16]

Materials.

The meta-dinitrobenzene was kindly supplied us by Andrews, Lynn and Johnston, and was of the same purity as the sample which they used in their determination of the heat of fusion by a method which involved the construction of the heat-content temperature curve for the substance.[17]

The chlorobenzene was a pure sample "for thermocouple calibration" supplied through the courtesy of Professor Jean Timmermans of the University of Brussels.

The meta-dichlorobenzene used was the middle fraction of a vacuum distillation of the product purchased from the Eastman Kodak Co. It still contained a small amount of impurity, as shown by a heating curve, its freezing point being − 25°. The impurity was not great enough to affect the results of these experiments appreciably as the compound was used only to prepare a 0.005 molal solution of dichlorobenzene in chlorobenzene.

Thus, assuming that this sample contained as much as 1% of impurity, which is hardly probable, the maximum error caused in

[15] It is of course true that this method involves the transfer of some heat to or from the sample and that usually a larger amount of the sample has to crystallize to raise the temperature to the freezing point, thus causing the sample to appear less pure if the length of the flat is taken as the only criterion of purity. A pure compound, however, should obviously give the same freezing point by this method as by the other.

[16] A little time may usually be saved by dropping the shield temperature to just below that of the melt when the two are only about a degree apart, and then starting the curve from this point.

[17] Andrews, Lynn and Johnston, *loc. cit.*

the final figure for the composition would be only 0.005 molal percent. If the impurity consisted mainly of the ortho and para isomers, as is quite likely, the error involved would be even smaller since the impurity would then have the same molecular weight and would lower the freezing point of the chlorobenzene to the same extent as the meta-dichlorobenzene.

Experimental Results.

Cooling and heating curves were run on approximately 0.5 gram samples of (I) pure chlorobenzene, (II) chlorobenzene containing 0.50 mole percent of meta-dichlorobenzene, and (III) a partially purified sample of chlorobenzene which happened to be available. Typical results given in Tables 1 and 2 are represented graphically in Figures 2 and 3 respectively.

In the tables, the columns labelled I, II and III give the temperatures of the corresponding samples at the times shown in the first column. The curves have been shifted along the time axis to make them more readily comparable; i. e., in Table 1, so that they all coincide at the time of initial crystallization when the temperature of the sample rises to the freezing point, and in Table 2, so that the shield temperatures of curves II and III lag about two minutes behind those for curve I. The figures in parenthesis are the temperatures of the shield. The temperatures are all given in microvolts as read, since the corresponding unit in degrees is an inconvenient figure, 0.0293° for readings between − 1600 and − 1700 microvolts. A calibration correction of − 1 microvolt must be added to the figures given so that the corresponding temperatures may be read directly from the standard conversion tables.[18]

In the graphical representations the shield temperatures for Curves I alone have been drawn (the heavy straight lines) since for practical purposes the slopes for the other two curves corresponding may be considered the same. In Figure 2 therefore they would all practically coincide and in Figure 3 the shield lines for samples II and III would both be represented by a line roughly parallel to that for sample I shown but with each point shifted about two minutes to the right.

The cooling curves obtained for chlorobenzene (sample I) showed that it was slightly purer than the meta-dinitrobenzene sample so that we have used the former as our standard for a pure substance.

[18] "International Critical Tables," New York, Vol. I, page 58.

TABLE 1.

Cooling Curves.

Time (min.)	I microvolts	II microvolts	III microvolts
10	1859	1853	1865
10.5	1647	1658	1675
11	1647	1655	1675
11.5	(1960)	(1977)	(1973)
12	1647	1655	1675
12.5	(1977)	(1988)	(1987)
13	1647	1655	1675
13.5	(1993)	(1999)	(2000)
14	1647	1655	1675
14.5	(2006)	(2013)	(2013)
15	1647	1655	1678
15.5	(2020)	(2027)	(2024)
16	1647	1656	1680
16.5	(2034)	(2042)	(2036)
17	1647	1659	——
17.5	(2049)	1660	1685
18	1647	1661	(2055)
18.5	(2062)	(2070)	1690
19	1647	1665	(2070)
19.5	(2075)	(2082)	1699
20	1648	1675	(2083)
20.5	(2092)	(2094)	1710
21	1648	1690	1717
21.5	(2104)	1699	1727
22	1651	1710	1735
22.5	1655	1722	1746
23	1660	1734	1756
23.5	(2136)	1752	(2123)
24	1690	1769	1784
24.5	1751	1786	1802
25	1797	(2152)	1828
25.5	(2165)	1835	1853
26	1887	1878	1875
26.5	(2178)	1897	(2165)
27	1970	1930	1922
27.5	(2195)	(2184)	(2180)
28	——	1975	1965
28.5	(2207)	(2197)	(2194)
29	——	2015	1997
29.5	——	(2208)	(2205)

TABLE 2.

HEATING CURVES.

Time (min.)	I microvolts	II microvolts	III microvolts
4.5	(1785)	——	——
5	1785	——	——
5.5	(1777)	——	——
6	1780	——	——
6.5	(1768)	(1781)	——
7	1775	1778	——
7.5	(1779)	(1775)	(1778)
8	1770	1776	1777
8.5	(1749)	(1764)	(1771)
9	1762	1770	1773
9.5	(1740)	(1758)	(1763)
10	1753	1765	1768
10.5	(1732)	(1751)	(1752)
11	1745	1757	1764
11.5	(1725)	(1743)	(1745)
12	1735	1753	1760
12.5	——	(1732)	(1736)
13	1727	1747	1755
13.5	(1708)	(1723)	(1728)
14	1718	1745	1751
14.5	——	(1716)	(1719)
15	1710	1739	1747
15.5	(1690)	(1709)	(1712)
16	1702	1734	1743
16.5	——	(1700)	(1705)
17	1692	1730	1739
17.5	(1672)	(1692)	(1696)
18	1683	1726	1735
18.5	——	(1683)	(1687)
19	1675	1721	1731
19.5	(1653)	(1675)	——
20	1671	1717	1727
20.5	——	——	(1671)
21	1666	1712	1725
21.5	(1635)	(1657)	(1661)
22	1662	1707	1721
22.5	(1628)	(1650)	——
23	1660	1704	1717
23.5	(1621)	(1641)	(1645)

TABLE 2.—*cont.*

Time (min.)	I microvolts	II microvolts	III microvolts
24	1658	1698	1714
24.5	(1612)	(1633)	(1636)
25	1657	1694	1710
25.5	(1603)	—	(1628)
26	1655	1690	1708
26.5	—	(1618)	—
27	1654	1686	1706
27.5	(1583)	(1607)	(1613)
28	1654	1684	1705
28.5	—	(1600)	(1605)
29	1653	1680	1701
29.5	(1570)	(1592)	(1598)
30	1651	1678	1700
30.5	(1563)	(1584)	—
31	1651	1676	1698
31.5	(1552)	(1577)	(1580)
32	1650	1674	1696
32.5	—	(1569)	(1570)
33	1650	1671	1695
33.5	(1534)	(1562)	(1561)
34	1650	1670	1693
34.5	—	(1554)	(1553)
35	1649	1669	1691
35.5	(1518)	(1546)	(1545)
36	1649	1667	1690
36.5	—	—	(1536)
37	1648	1665	1688
37.5	(1501)	(1530)	(1527)
38	1648	1664	1687
38.5	—	(1522)	(1518)
39	1648	1662	1685
39.5	(1483)	(1514)	(1512)
40	1648	1661	1684
40.5	(1475)	(1506)	(1505)
41	1647	1661	1682
41.5	(1468)	(1498)	(1499)
42	1647	1660	1681
42.5	(1460)	(1490)	(1492)
43	1646	1658	1681
43.5	(1450)	(1481)	(1484)

TABLE 2. *–cont.*

Time (min.)	I microvolts	II microvolts	III microvolts
44	1646	1657	1679
44.5	(1437)	(1471)	(1475)
45	1645	1656	1678
45.5	——	(1461)	(1468)
46	1645	1655	1677
46.5	(1416)	(1451)	(1461)
47	1645	1655	1676
47.5	1645	(1442)	1676
48	1643	1655	1676
48.5	1641	1654	1675
49	(1395)	1652	1673
49.5	1639	1650	1670
50	1635	1648	1667
50.5	1632	1646	1665
51	1630	1643	1660
51.5	(1377)	(1404)	(1420)
52	1618	1632	1650
52.5	(1365)	(1397)	(1410)
53	1597	1604	1633
53.5	1582	(1390)	(1401)
54	1557	1524	1596
54.5	(1353)	(1383)	(1391)
55	1510	1471	1558
55.5	(1346)	(1376)	(1382)
56	1465	——	1517
56.5	(1339)	——	(1373)
57	1432	——	——
58	1404	——	——
58.5	(1320)		

Comparison of the Time-Temperature Curves.

A comparison of the results obtained for samples I, II and III (see Figures 2 and 3) shows that *the effect of impurity on the shape of the cooling and heating curves is much more pronounced when the compound is very nearly pure.* Thus, the effect of the first 0.5 molal percent added to the pure compound was almost as great as over three times as much impurity.

Cooling Curves. Curve I, Figure 2, shows the type of cooling curve obtained with the purest sample of chlorobenzene. From minute

10.5 to minute 21, the fall in temperature is only one micro-volt. The temperature falls 35 microvolts during the next three minutes and then drops abruptly and practically linearly toward the shield temperature. The maximum rate of fall is reached at about the 24th minute.[19]

Although the freezing point of sample II is only about 8 microvolts, 0.23° C., lower than that of the pure standard the characteristics of the cooling curve (Curve II, Figure 2) have been very decidedly altered. (1) The "flat", that is, the constancy of the temperature to within one microvolt, lasts only about one-half as long, from minute 10.5 to minute 16. (2) The subsequent falling off of the temperature is much more gradual so that the maximum rate of drop is not reached until about 9 minutes later. (3) The drop to the temperature of the shield is less steep, and therefore (4) this part of the curve has a fairly definite point of inflection not perceptible in Curve I, and (5) Curve II crosses Curve I.

Although Sample III contains enough impurity to lower the freezing point of the pure standard about three and one-half times as much, 29 microvolts (0.85° C), as in the case of Sample II, the characteristics of the cooling curve (Curve III, Figure 2) are not very different. The "flat" still lasts 3.5 minutes, from minute 10.5 to minute 14, the rounding off of the curve from this point is only a little more decided, and the drop to the temperature of the shield is only slightly slower so that in this region it runs almost parallel to Curve II though they finally do cross. Here also the maximum rate of fall of the temperature is at about the 24th minute.

Necessity for Sufficient Supercooling. It must be kept in mind that during the cooling curve the sample is never in true equilibrium except immediately after the crystallization causes the rise in temperature of the supercooled liquid to the freezing point. At this point only is the sample at the same temperature throughout. In the absence of stirring,[20] the part of the sample next to the walls of the tube

[19] Curve I (Figure 2) and Curve I (Figure 3) are quite satisfactory approaches to the ideal cooling and heating curves for a pure substance. For a thorough discussion of the reasons for the deviations from these ideal curves in practice, the reader is referred to papers by White [Amer. Jour. Sci., [4], *28*, 453 (1909); Z. anorg. Chem., *69*, 305 (1911); and J. Phys. Chem., *24*, 393 (1920)]. See also Andrews, Kohman and Johnston, *loc. cit.*, Steiner and Johnston, J. Phys. Chem., *32*, 914 (1928), and Tammann, "Aggregatzustände," Leipzig (1922).

[20] White, J. Phys. Chem., *24*, 393 (1920), pointed out that the necessity for stirring can be escaped, and to advantage, by using a sample tube of small diameter.

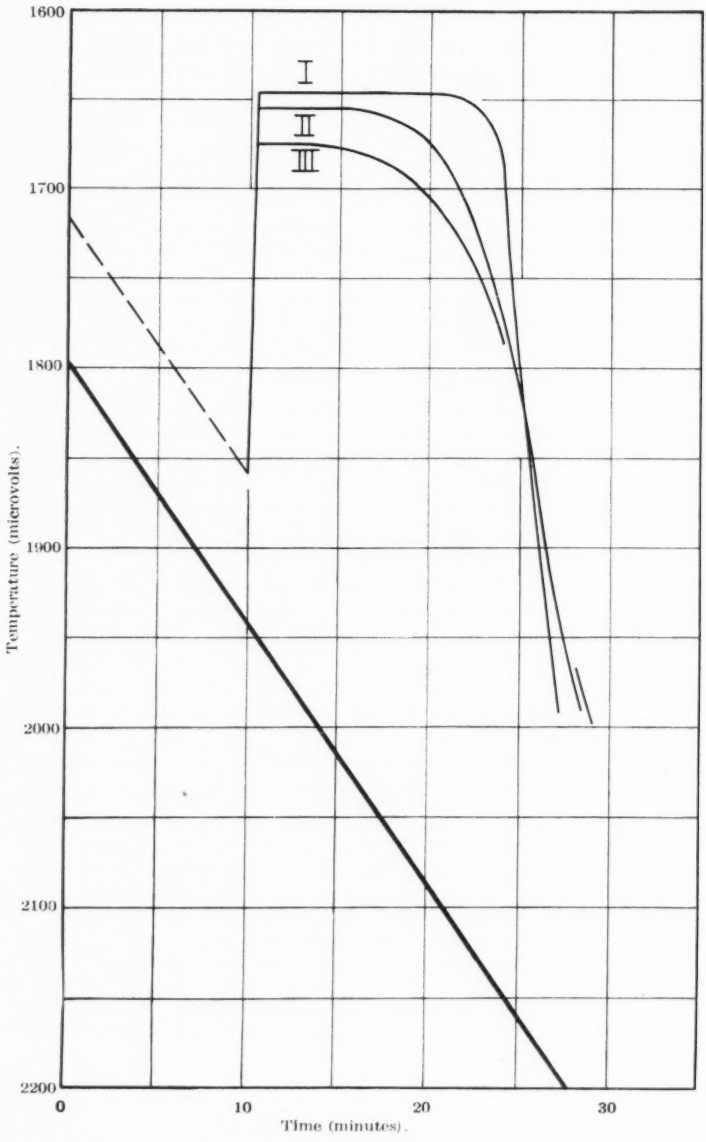

FIGURE 2. Cooling Curves.

freezes further and thus forms a solid shell around the sample, a shell which then cools below the freezing point and therefore conducts the heat away from the layer immediately inside so that that likewise freezes completely, giving up its heat of fusion, and becomes a part of the outer conducting shell. The temperature at the center of the sample remains constant until the shell has grown in that far.

In some cases the crystals formed may segregate at the top or at the bottom of the sample, depending on the relative densities of the liquid and solid phases, and then grow downwards or upwards as the case may be. The resulting cooling curves are of course abnormal and erratic. To avoid such a condition it seems better to use a rather large degree of supercooling so that enough crystals are formed at once to form a network throughout the liquid, thus preventing segregation at the top or the bottom.[21]

Heating Curves. The type of heating curve obtained with the purest sample of chlorobenzene is shown by Curve I (Figure 3). After the first few minutes the temperature of the melt rises parallel to that of the shield (represented by the heavy straight line) and at about minute 19 there is a fairly sharp rounding off after which the temperature of the sample rises more and more slowly until, between minute 35 and minute 47.5, the rise is only 4 microvolts. There is then a decided rise toward the temperature of the shield.

It should be noted particularly that *the first signs of melting appear approximately at the time when the shield reaches the temperature of the "flat."* This is exactly the behavior which would be expected for a pure compound considering the conditions under which the heating curve was obtained.[22] In comparing this curve with those for the samples

[21] When the supercooled liquid is very viscous, as is usually the case for substances freezing at low temperatures, the crystals cannot be efficiently mixed with the liquid as a whole and one has to depend on the growth or propogation of the first crystals formed. The rate of this propogation increases with the degree of supercooling until a maximum rate is reached considerably below the freezing point. It should also be noted that, especially with low rates of crystallization, for an impure substance there may be a partial segregation of impurities in the portions remaining liquid longest. See Tammann, "Kristallisieren und Schmelzen," Leipzig (1903) pages 131–137.

[22] During such a curve, there is a temperature gradient from the outside of the sample to the thermocouple in the center, and the outside reaches the melting point first, shortly after this temperature has been reached by the surroundings. The outer layer of solid then liquefies and gradually grows toward the center where the temperature of the sample is being measured. See White, *loc. cit.*, and Tammann, *loc. cit.*

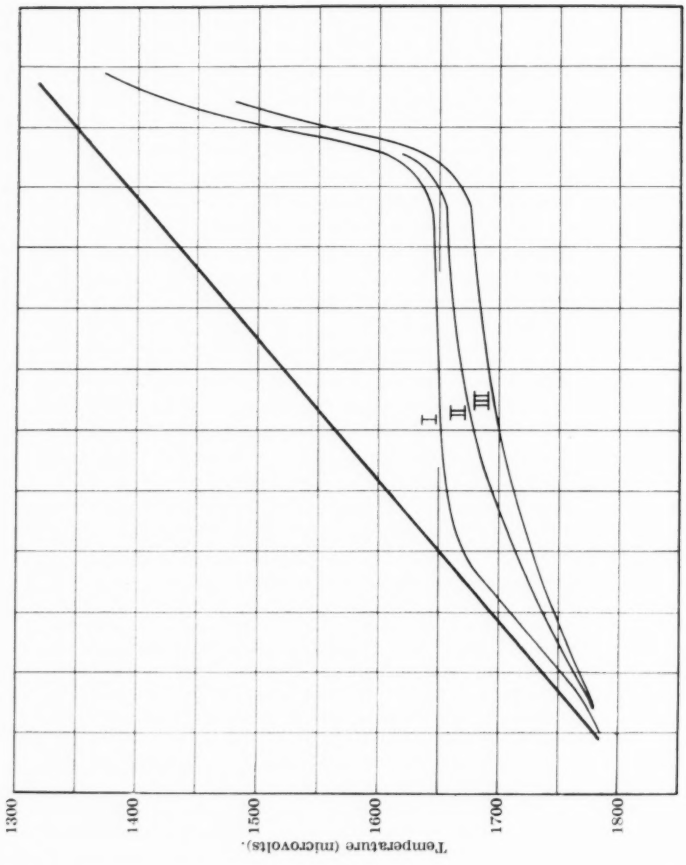

FIGURE 3. Heating Curves.

containing impurity[23] (Curves II and III, Figure 3), three important differences are obvious. (A) The temperature of the impure samples does not tend to follow that of the shield exactly but continues to digress from it from the very beginning and increasingly so,[24] thus causing the approach to the flat to be much more gradual. (B) The constancy within four microvolts just before the final break lasts in Curve II for only 5.5 minutes, from minute 43 to minute 48.5, (as compared with 12.5 for Curve I), and in Curve III for 4.5 minutes, from minute 44 to minute 48.5. (C) The break at the end of the slow rise seems in each case to come within 2 microvolts of the freezing point as determined by the corresponding cooling curves. This will be discussed further below. In the case of effect (A) and (B) it should be noticed that, as in the case of the corresponding cooling curves, there is almost as great a difference between Curves I and II as between I and III although the percentage of impurity in III is roughly three times as great as in II.

Specifications for Cooling and Heating Curves for a Pure Compound.

On the basis of the above experiments the following are the important characteristics of cooling and heating curves, obtainable under the same conditions in this or a corresponding apparatus, which are suggested for use in applying this method as a criterion of purity using the pure chlorobenzene as a standard.

Cooling Curves. (1) The "flat," that is, that portion of the curve where the temperature drops through only one microvolt, should last through three-quarters of the time between the initial crystal-

[23] In making this comparison it should be kept in mind that all the points for the shield and the melt temperatures have been shifted to the right about two minutes in the case of Curves II and III, in both the tabulation (Table 2) and the graphical representation (Figure 3).

[24] This is exactly what would be expected since the specific heat of the impure sample increases rapidly with the temperature in the region just below the melting point (see White, *loc. cit.*). On the basis of Newton's Law of Cooling and the conditions under which these curves were obtained, it can be shown theoretically that the difference between the shield temperature, θ_s, and the melt temperature, θ_m, should be proportional to the specific heat of the sample, so that the value for $(\theta_s - \theta_m)$ reached would remain practically constant up to the melting point for a pure compound, whereas the presence of impurities would cause a gradual increase in $(\theta_s - \theta_m)$ in this range as here observed.

lization and the time when the melt temperature has reached its maximum speed downwards. (2) Within the three minutes following, the temperature should drop at least 1° (about 35 microvolts). For substances having a very low heat of fusion per gram, the temperature difference between the shield and the sample as measured at this point would be much smaller and therefore the drop during the next three minutes would be correspondingly smaller. This condition would, however, be indicated by a much shorter duration of the whole curve. (3) The ensuing drop to the temperature of the shield should be very rapid and almost linear when plotted on a scale of 2.5 minutes and 25 microvolts to a centimeter.

The presence of impurities is indicated by a shorter flat which is followed by a much more gradual drop to the maximum rate of fall. This maximum rate is less rapid than in the case of a pure compound and this part of the curve shows a more or less distinct point of inflection.[25]

Heating Curves. (1) The temperature of the sample should soon assume a practically constant rate of rise equal to that of the shield and in the case of an *extremely* pure sample should not deviate therefrom before the temperature of the *shield* has reached the melting point. (2) The "flat," with a constant temperature within five microvolts, should last through about one-half of the period during which actual melting is taking place. If the substance has a very low heat of fusion per gram this "flat" may be much shorter; thus, this criterion alone is not as conclusive as the approach to the "flat."

If the sample is not pure, the temperature of the sample does not rise parallel to that of the shield. Its rate of change grows increasingly less than that of the shield and thus the curve is much more rounded in its approach to the "flat," which is shorter than for the pure compound.

The Advantages of Heating Curves over Cooling Curves as a Criterion of Purity.

The above results seem to indicate that heating curves are perhaps to be preferred to cooling curves in testing the purity of a compound.

In the first place, they are more easily obtained since the procedure is more automatic, there being no necessity for the rather troublesome supercooling, inoculating and stirring.

[25] The "flat" in this case is of course lower than for the pure compound but this cannot be observed from the one curve alone. The same is true for the heating curves.

Secondly, they have a wider range of applicability, for in the case of some compounds it is impossible to get normal cooling curves on account of their failure to crystallize at the proper time or on account of their slow rate of crystallization.[26] On the other hand, it is always possible to get a heating curve of a compound if it can be made to crystallize at all.

Thirdly, heating curves are probably more sensitive to very small amounts of impurities, for in the range just below the freezing point, where the impurities have the greatest effect on the specific heat, deviations from the normal curve for a pure compound can be much more readily and definitely detected because (1) the difference between the shield and the melt temperatures is only a degree or two instead of in the neighborhood of twenty degrees as in the case of the cooling curves and (2) the curve for the shield supplies the comparison line for the pure compound whereas in the corresponding range for the cooling curve, the sharp drop at the end, the slope of the reference line representing the pure compound can not be very definitely described.

Fourthly, in the case of compounds which transform as soon as they liquefy and where, therefore, the use of the cooling curve method is out of question, the heating curve method is, in some cases at least, still quite practicable; for example, in the case of transanisaldoxime.[27] This is undoubtedly due to the fact that during a heating curve the transformation takes place only in the melted portion which grows inwards from the outside of the sample tube and that the temperature gradient in the solid core remaining for the duration of the melting is therefore not greatly affected.

Limitations of the Heating Curve and Cooling Curve Methods.

If the heating curve obtained for a sample by this method gives indications of impurities, the presence of impurities is quite definitely proved. It has been our experience, however, that the same state-

[26] This happens much more often for liquids than for solids. It was shown by Tammann and Hesse, Z. anorg. allg. Chem., *156*, 245 (1926), that the higher the melting point, the greater is the temperature interval in the supercooled liquid state within which the working of the viscous mass by blowing, drawing, etc. is possible; that is, within which it may be expected to attain equilibrium between the liquid and the solid phases with the most efficient stirring.

[27] Skau and Saxton, J. Phys. Chem., January, 1933.

ment can not be made unconditionally for cooling curves, as these are much more likely to show abnormalities due, for example, to the effectiveness of the inoculation and to the ease with which the supercooled liquid crystallizes, as will be discussed below.

As has been pointed out before, however,[28] if a sample gives a cooling curve or a heating curve which corresponds with that for a pure compound, the proof that the sample is pure is still not absolutely established. It can merely be stated that the composition of the solid phase and of the liquid phase remain identical throughout the freezing or melting, and therefore the possibility of a eutectic mixture and of certain supposedly rare mixed-crystal types are not excluded. Ordinarily, however, enough is known about the sample from other data to reduce the probability of its being a mixture of such exact composition as, for example, a eutectic mixture.

Determination of Freezing Points or Transition Points.

The freezing point of a sample can theoretically be found directly from the cooling curves or heating curves which have been run to test its purity. Further, it can usually be read much more easily from the cooling curve than from the heating curve due to the fact that in the former case the temperature remains constant at the freezing point for a considerable length of time, at the beginning of which the solid and liquid phases are presumably in true equilibrium. In the case of heating curves, on the other hand, the temperature is not perfectly constant, nor is the sample as a whole at equilibrium at the time the freezing point is reached. In fact, in the latter case the exact point taken as the freezing point has to be more or less empirically chosen; on the basis of this and of considerable unpublished work the temperature of the sample two minutes before the beginning of the change in direction of the curve at the end of the "flat" can be taken as the freezing point.

In general it has been our experience that if crystallization takes place rapidly[29] the values obtained by the two methods agree within two or three microvolts, the value for the heating curve almost always

[28] The reader is referred to a paper by E. W. Washburn [Jour. Ind. Eng. Chem., *22*, 985 (1930)] in which various criteria of purity are discussed.

[29] In such cases the process of purification, during a fractional distillation, for example, can be followed by freezing point determinations, of the type described below, until successive fractions show only slight differences, and then the shape of the completed curves can be determined for the final fractions.

being the higher. Thus, in the case of Samples I, II, and III, the values are −1645, −1655, and −1676 microvolts, respectively, by the heating curves, and −1647, −1656, and −1675 by the cooling curves. It is not conceivable that the freezing point obtained from the cooling curve can be too high since the surroundings are always at a lower temperature than this and the sample approaches the freezing point from a lower temperature. On the other hand, the value obtained from the heating curve seems never to be too low.[30] [31] Thus, in this case, for example, we can say the freezing point of pure chlorobenzene lies between −1645 and −1647 microvolts, −45.20° and −45.26°. This agrees well with the value assigned to it by Timmermans, −45.2°.[32]

The agreement between heating and cooling curves is not always as good as in the above case, however, and it is usually the cooling curve value which is at fault. The value from heating curves is usually reproducible to within two microvolts at least and, on the other hand, no general statement can be made in regard to the reproducibility obtainable from cooling curves except that it is dependent on a fairly rapid rate of crystallization under the conditions of these experiments.[33] When the substance crystallizes much too slowly under the given conditions, as often happens, the apparent freezing

[30] This was pointed out, for example, by White, *loc. cit.*; see also Tammann, "Aggregatzustände."

[31] The fact that the cooling curve for sample III gave a value which was higher than that for the heating curve can not be considered as an exception to this statement since the difference was only one microvolt, and therefore within the accuracy of our readings.

[32] Timmermans, van der Horst and Onnes, Archives Neerlandaises des Sciences Exactes et Naturelles, III A, *6*, 180 (1922). See also Communications from the Physical Laboratory of the University of Leiden, Supplement No. 51b, page 35 (1924). The more recent value of Timmermans, −45.35° [Timmermans, Communications from the Physical Laboratory of the University of Leiden, Supplement No. 84 page 3 (1928)] has been retracted by him in favor of his previous value. (Private Communication.)

[33] It should be remembered that this crystallization takes place without vigorous stirring and that therefore if the supercooled liquid is viscous it is more difficult to attain the true equilibrium temperature between the solid and liquid phases. Even in the case of chlorobenzene, Sample I above, where the crystallization takes place rapidly, one of the cooling curves gave a value of −1649 instead of −1647 microvolts. The shape of the curve, however, is not perceptibly different so that its use as a criterion of purity is not affected.

point may vary from curve to curve and the shape of the curves may indicate a high percentage of impurity even though the substance is pure.

In determining the freezing point by cooling curves, therefore, a number of rapid curves should be run on the sample, setting the shield temperature at intervals of 50 or 100 microvolts below the freezing point for successive curves, inserting the melted sample in the apparatus, and starting the crystallization when the temperature of the melt has come to within 50 or 100 microvolts of that of the shield, which should be kept roughly constant. Thus, various degrees of supercooling can be tried and the highest value obtained for the freezing point will obviously be the nearest to the true value. Four such determinations can usually be carried out in a half hour, since the curves do not have to be completed; the sample being remelted outside the apparatus and a new curve started as soon as the temperature of the beginning of the "flat" has been measured. The freezing points obtained by this method would of course not be expected to be accurate if much impurity were present.[34]

If the original cooling and heating curves give freezing points which agree within one or two microvolts, the true freezing point can be taken as the mean of these values. If, as often happens, the difference is greater, the true freezing point must lie between the heating curve value and the highest value obtained from a series of rapid cooling curves; and if the difference is very decided or if the cooling curve values do not agree among themselves, the true freezing point probably lies nearer the heating curve value.

The same type of curves can be run to find the transition temperature of one solid form into another, but in this case, as has been previously been pointed out for the case of carbon tetrachloride,[35] the cooling curve method is much more likely to give low results than in the case of a solid-liquid equilibrium.

Discussion.

As was pointed out by Washburn,[36] we can never be absolutely certain that a given compound is pure; we can merely reduce the probability of its being impure to a minimum. Let us consider from this point of view the advantage of the time-temperature-curve method for detecting impurity.

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[34] Nernst, Z. physik. Chem., *15*, 681 (1894).

[35] Skau and Meier, Jour. Amer. Chem. Soc., *51*, 3517, (1929).

[36] Washburn, *ibid.*

If a liquid has been purified by fractional distillation, and finally a sample has been obtained which boils at a constant temperature, and which, on further fractionation, gives fractions all of which have this same boiling point, we can conclude that the sample is either a pure compound, an azeotropic mixture, or an ideal solution of two or more substances having identical boiling points; and that thus the probability that it is impure is equal to the probability of it being a constant-boiling mixture. This probability can not be reduced by showing that other physical constants also are identical for the various fractions, or, in other words, by applying any number of additional comparative criteria, except insofar as these constants may be more sensitive to impurity than the boiling point; another method of fractionation may now be resorted to, e. g., fractional crystallization without a solvent. If the fractions thus obtained are identical so far as the physical constants are concerned we can state that the sample is either a pure compound or, that which is highly improbable, that it is a constant-boiling mixture which freezes completely at a constant temperature.[37]

The same degree of certainty in regard to purity may be obtained much more simply by the use of a non-comparative method; for example, by showing that the original sample which boils at a constant temperature gives time-temperature curves corresponding to those for a pure compound. In other words, the occurrence of this type of time-temperature curve indicates at once that the sample freezes at a constant temperature and thus obviates the necessity of carrying out the fractional crystallization which had to be resorted to in the other case in order to reach approximately the same degree of certainty.

Advantages of the Apparatus. The following are the outstanding advantages of the apparatus here described for use as a criterion of purity: (1) It is applicable to both liquids and solids.[38] (2) The sample necessary is very small, 0.5 to 0.7 grams. (3) The sample is always visible. (4) The samples can be handled entirely in vacuo in permanent sample tubes and contamination is thus impossible. This

[37] Since the composition of the solid phase must be the same as that of the liquid out of which it has crystallized.

[38] It has also been used for determining the freezing point and the purity of samples of substances which are gases at room temperature, which were supplied to us through the kindness of Dr. H. S. Davis. See Davis and Schuler, Jour. Amer. Chem. Soc., *52*, 721 (1930).

is of great importance not only in the case of compounds which are hygroscopic (like ethyl alcohol) or which absorb carbon dioxide from the atmosphere (like certain amines) or which oxidize in air (like polyphenols), but also in the case of any liquid freezing below 0° C., for at low temperatures the condensation of moisture and of carbon dioxide as well as the solution of air in the sample are very grave sources of contamination. (5) The complete time-temperature curve can be measured and thus the shape of the curve rather than just the length of the "flat" is obtainable. (6) Any number of determinations can be made on the same sample. (7) The curves obtained should be readily reproducible by other investigators. Since the temperature gradient and rate of temperature fall can be designated and since stirring is unnecessary, the conditions can be quite exactly defined. (8) The apparatus has been "calibrated" for use as a non-comparative criterion of purity using as a standard a sample which was proved by its temperature-heat-content curve to be sufficiently pure. (9) The apparatus can be used for the determination of freezing points and transition points with an accuracy of a few hundredths of a degree.

Acknowledgement.

This opportunity is taken to thank Professor Frederick G. Keyes for the kind interest he has taken in this investigation.

Summary.

An apparatus for obtaining time-temperature curves has been described in which the sample may be handled in vacuo if desired. The interpretation of the curves obtained with this apparatus (1) as a criterion of purity and (2) for accurate freezing point determinations have been discussed on the basis of experimental curves for a standard sample of high purity as well as for samples containing known amounts of impurity, and the advantages of heating curves over cooling curves have been pointed out. Criteria of purity have been classified as comparative and non-comparative criteria and the relative merits of the two classes have been discussed.

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